

Short communication

Single-stage temperature-controllable water gas shift reactor with catalytic nickel plates



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HIGHLIGHTS

- A new single-stage temperature-controllable reactor was developed for the exothermic WGS reaction.
- CO conversion increased to its equilibrium value at 375 °C with a CH₄ selectivity of <0.5%.
- The heat generated from the WGS reaction was sufficiently controlled with the coolant flow rate.

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ABSTRACT

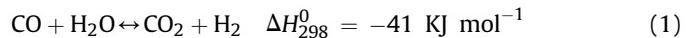
In this study, a microstructured reactor with catalytic nickel plates is newly designed and developed for proper heat management in an exothermic water gas shift WGS reaction. The reactor is designed to increase the reactor capacity simply by numbering-up a set of a catalyst layers and heat exchanger layers. The WGS reactor is built up with two sets of a catalyst layers and heat exchanger layers. The performance of the reactor is verified by WGS testing with the variation of the furnace temperatures, gas hourly space velocity (GHSV) and coolant (N₂) flow rate. At a GHSV of 10,000 h⁻¹, CO conversion reaches the equilibrium value with a CH₄ selectivity of ≤0.5% at the furnace temperature of ≥375 °C. At high GHSV (40,000 h⁻¹), CO conversion decreases considerably because of the heat from the exothermic WGS reaction at a large reactants mass. By increasing the coolant flow rate, the heat from the WGS reaction is properly managed, leading an increase of the CO conversion to the equilibrium value at GHSV of 40,000 h⁻¹.

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1. Introduction

The growing energy demand has caused the depletion of oil reserves and an increase in CO₂ emission. Consequently, the need for the development of clean energy technologies has increased. Hydrogen is considered a promising clean energy carrier, and the environment-friendly hydrogen production technologies from coal and natural gas have been developed in the last decade. At present, the annual world hydrogen production is approximately 45–50 million tonnes, corresponding to approximately 2% of the primary energy demand [1,2]. The largest consumption of hydrogen is in petroleum refining and petrochemical industries for ammonia and

methanol synthesis [3]. Most of the hydrogen (~96%) is produced by steam reforming of natural gas and gasification of coal and biomass [4,5]. In the case of the use of fossil fuels as hydrogen sources, carbon dioxide capture and storage is an important issue in the hydrogen production route. The stream that is emitted by a reformer or gasifier contains 10–60% CO (dry basis), which can be further converted to CO₂ and H₂ through the water gas shift (WGS) reaction (Eq. (1)). Then, CO₂ capture and high purity H₂ production is simultaneously accomplished by H₂/CO₂ separation through liquid phase solvents for which both physical solvents (e.g., Selexol) [6], chemical solvents (e.g., amines) [7] and hydrogen selective membranes [8] are used.



In traditional applications, the CO conversion process has multi-stage WGS reactors. The first of these reactors is a high-

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temperature shift (HTS) reactor that is operated at high temperature ($350\text{--}400\text{ }^{\circ}\text{C}$) under a Fe–Cr based catalyst [9–11], and the second one is a low-temperature shift (LTS) reactor that is operated at a low temperature ($\sim 200\text{--}300\text{ }^{\circ}\text{C}$) under a Cu–Zn based catalyst [12–14]. Like other chemical reactors, proper heat management is a key issue in the WGS reactor for efficient use of catalyst. This reaction is exothermic and reversible, and there is no variation of the mole number. Therefore, CO conversion is thermodynamically favoured at low temperatures, and the pressure does not affect the conversion in traditional reactors. Because the exothermal WGS reaction causes the reactor temperature to rise, integrated heat removal is needed to maintain the isothermal operation and thus, high CO conversion. In typical industrial applications, the multi-bed adiabatic reactors with interstage cooling for exothermal reversible reactions are suggested to ensure sufficiently high CO conversion [6,15,16]. There are new designs for compacting the WGS reactor by applying active heat exchange or heat distribution in monolith or micro-structured reactors [17–20]. These reactors are composed of metallic thin plates and allow for isothermal operation or operation with a minimised temperature gradient.

Recently, we developed a novel catalytic nickel plate for the production of synthetic natural gas [21] and steam reforming of methane [22]. The advantages of the catalytic nickel plate are: i) a hydrogen selective membrane effect that allows the system to surpass the equilibrium conversion, ii) a super mass transfer through the sub-micron channel formed in the membrane structure, and iii) a super heat transfer and re-distribution throughout the thin metal plate. Hwang et al. modified the catalytic nickel plate with potassium and showed a good performance in the HTS reaction [23].

In this study, a newly designed microstructured reactor with catalytic nickel plates was developed for proper heat management in an exothermal reaction. The HTS reaction test was carried out under very severe experimental conditions ($\text{GHSV} = 40,000\text{ h}^{-1}$) with the variation of coolant flow rate to manage the heat from the exothermal WGS reaction.

2. Experimental

2.1. Catalytic nickel plate and reactor design

The catalytic nickel plate was made using the sintered metal method developed by KIER [21,22] and modified with potassium for a good performance of the WGS reaction, as shown in the previous study [23]. The reactor was newly designed to control the temperature of the catalyst bed on a single stage because the WGS reaction is exothermic and can generate a great amount of heat causing catalyst deactivation and side reactions, such as methanation. As shown in Fig. 1, the designed MCR consists of cover plate, catalyst layers, reactant distribution layers, product collection layers and heat exchanger layers. The reactor capacity of the WGS reaction can be increased by numbering up a set of layers that includes a catalyst layer, a reactant distribution layer, a product collection layer and a heat exchanger layer. All of the layers are made of metal sheets. The catalyst layer is composed of a catalyst holding plate and a catalytic nickel membrane. Several micron-sized channels are patterned on the product collection plates and heat exchanger plates. To distribute the reactant in the catalytic nickel membrane, 3-D channels are formed on the reactant distribution layer. The reactant inlet and the coolant outlet tubes and the coolant inlet and product outlet tubes are welded onto the cover and the bottom plates, respectively. Each plate is stacked alternately and then bonded by diffusion bonding method.

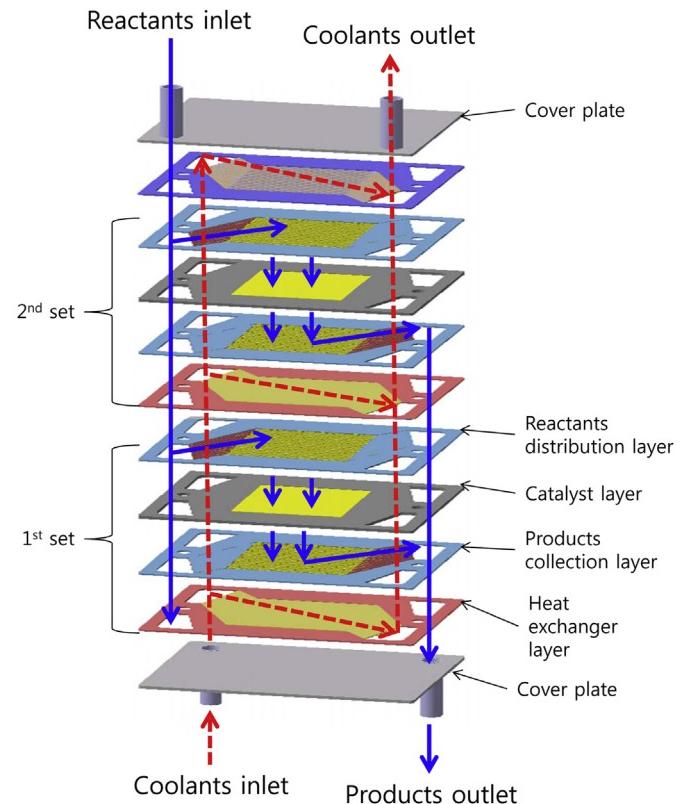
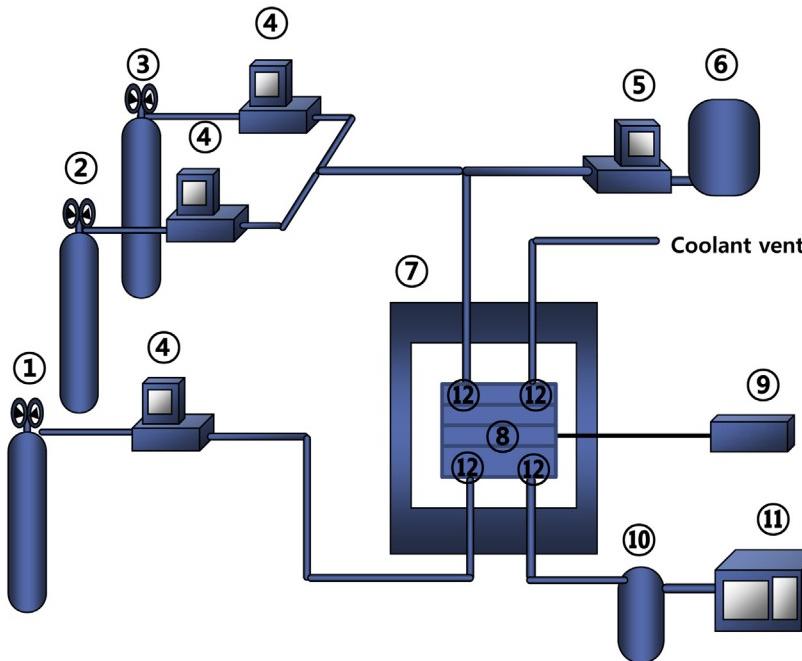


Fig. 1. The schematic representation of the newly designed single-stage temperature-controllable reactor and flow paths. Blue solid line: reactant and product flow path; Red solid line: coolant flow path. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. WGS test

The schematic of the WGS test is shown in Fig. 2. The WGS reactor was heated in an electric furnace equipped with a programmable temperature controller. The temperature of the furnace was controlled by a K-type thermocouple placed on the outside of the reactor, and the temperatures in the reactant inlet, product outlet, coolant inlet and coolant outlet were monitored. Nitrogen was supplied by a mass flow controller into the coolant inlet tube. As reactants, hydrogen and carbon monoxide were supplied by a mass flow controller (MFC, Brooks 5850 series), and liquid water was supplied by a micro liquid pump (NS, MINICHEMI PUMP). The WGS test was performed with a 60 vol.%CO + 40 vol.%H₂ mixture of gas with an H₂O/CO molar ratio of 3. The feed gas composition is similar to the gas composition of the coal gasifier [24], which is a more severe condition compared with the reformatte gas that arises from the steam reforming of methane [22]. The effect of temperature on the CO conversion was investigated at the temperature range of $300\text{--}450\text{ }^{\circ}\text{C}$ with gas hourly space velocity (GHSV) of $10,000\text{ h}^{-1}$. During the test of the temperature effect on CO conversion, N₂ of $0.12\text{ Nm}^3\text{ h}^{-1}$ was introduced. To see the reactor capacity, the GHSV was verified from 5000 to $40,000\text{ h}^{-1}$ at a furnace temperature of $375\text{ }^{\circ}\text{C}$. The reactor temperature is expected to rise under high GHSV because the WGS reaction is exothermic. The effect of the coolant's flow rate was performed under GHSV of $40,000\text{ h}^{-1}$ at $375\text{ }^{\circ}\text{C}$ to verify the performance of the newly designed WGS reactor for proper heat management. The product gases were analysed by a gas chromatograph (Agilent 6890N) equipped with HP-MOLSIV and HAYESEP D columns and thermal conductivity detectors (TCD). The surplus water in the products was separated by a cold trap before analysing the product gases.



1	N₂ gas tank	7	Furnace
2	CO gas tank	8	WGS reactor
3	H₂ gas tank	9	Temperature controller
4	Mass flow controller (MFC)	10	Cold trap
5	Water pump	11	Gas chromatograph (GC)
6	Water bottle	12	Temperature monitoring points

Fig. 2. Schematic of the WGS reaction experimental set-up.

The CO conversion and methane selectivity were calculated using the following equations:

ring, and the catalyst layer was 8.5 mm in thickness. Each heat exchanger layer composed of 18 channels had a flow path with

$$\text{CO conversion (\%)} = (\text{moles of CO consumed}/\text{moles of CO fed}) \times 100 \quad (2)$$

$$\text{CH}_4 \text{ selectivity (\%)} = (\text{moles of CH}_4 \text{ produced}/\text{moles of CO consumed}) \times 100 \quad (3)$$

3. Results and discussion

3.1. The newly designed WGS reactor

Fig. 3 shows the assembled WGS reactor. The WGS reactor was made of stainless steel 316 L plates and tubes. The reactor, as shown in Fig. 3(a), was composed of eight heat exchanger layers, two catalyst layers and four tubes. Four tubes were the reactant inlet, the product outlet, the coolant inlet and the coolant outlet. Each catalyst layers was separated by four heat exchanger layers, having a thickness of 1.0 mm. The dimensions of the catalytic nickel plate were 50 mm in diameter and 0.5 mm in thickness. The catalytic nickel plate was mounted on the assembly of the catalyst layer (in Fig. 3(b)). The assembly of the catalyst layer was composed of a product discharger, a catalyst support and catalyst holders. The catalytic nickel plate was tightened with a metal O-

the following dimensions: 1300 μm diameter, 250 μm depth and 35.5 mm length. The dimensions of the assembled reactor through the diffusion bonding method in INNOWILL Corp. were 80 mm × 60 mm × 30 mm, including two cover plates with a thickness of 2.0 mm.

3.2. WGS activity

The performance of the newly designed WGS reactor was verified by measuring the catalytic activity as a function of the furnace temperature at a GHSV of 10,000 h⁻¹. The furnace temperature was increased from 350 °C to 450 °C with a coolant (N₂) flow rate of 0.12 Nm³ h⁻¹. The results are presented in Fig. 4 with the thermodynamic equilibrium value of CO conversion. The CO conversion increased from 30% to its equilibrium value when the furnace temperature increased from 300 °C to 375 °C. At the furnace

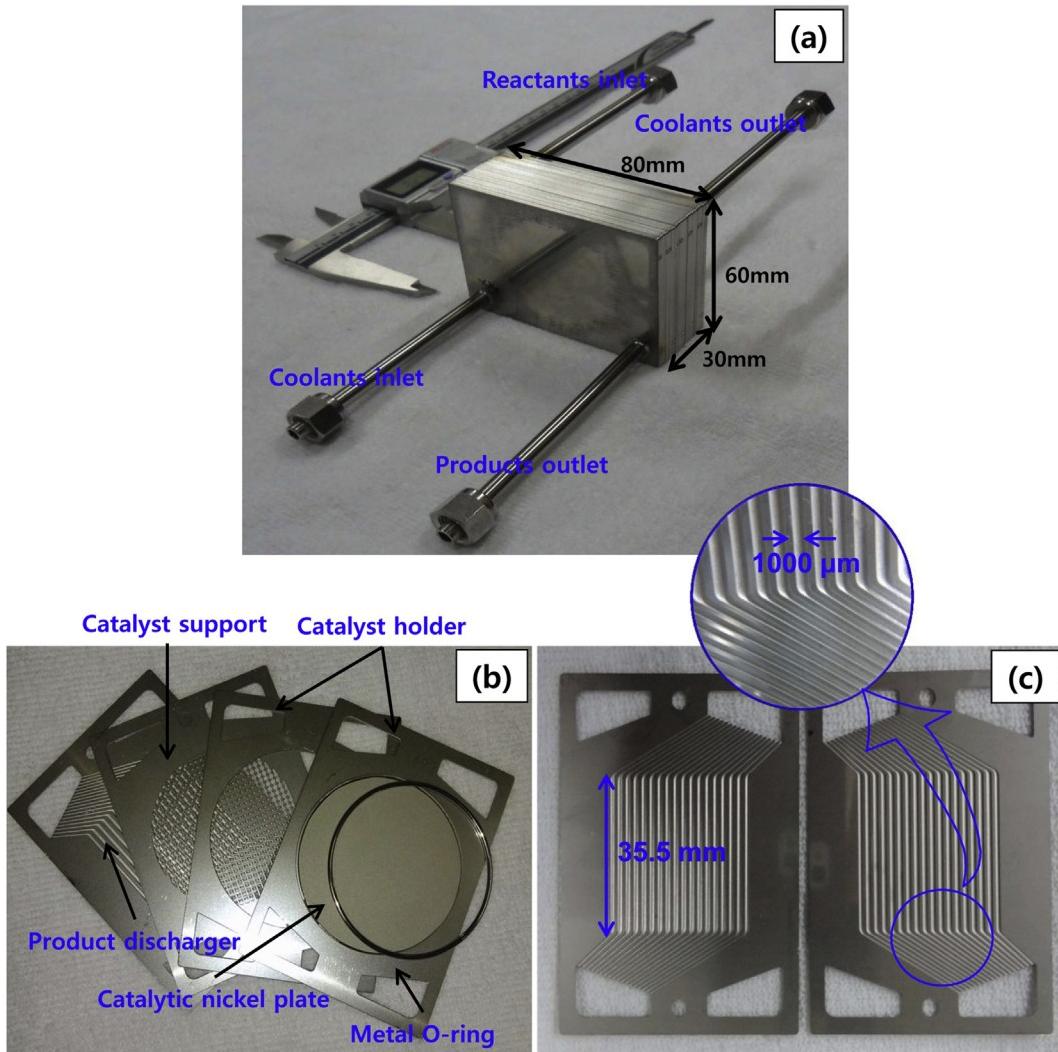
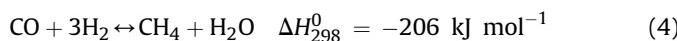


Fig. 3. Assembled WGS reactor (a), a pair of catalyst layers (b) and a pair of heat exchanger layers (c).

temperature of ≥ 400 °C, the CO conversion slightly exceeded even the equilibrium value. Methane can also be formed in the reactor from the reverse steam reforming reaction, i.e., methanation (Eq. (4)).



CH_4 is an undesired species in the product stream, and its formation results in the loss of two H_2 molecules for every CH_4 molecule produced, resulting decrease in the yield of H_2 production. It is well known that the Ni-based catalyst is very good in the methanation reaction, and it has been commercially developed for the production of synthetic natural gas (SNG) from coal and dry biomass [21,25]. Wheeler et al. [26] reported that the CH_4 selectivity increased rapidly from 0 to $\sim 5\%$ as the temperature increased from 200 °C to 550 °C under a $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst. The CH_4 selectivity calculated with Eq. (3) is displayed in Fig. 4 with a bar chart. The CH_4 selectivity increased with the increasing furnace temperature and reached 1.43% at 450 °C. However, the CH_4 selectivity remained very low at $\leq 0.5\%$ at the furnace temperature of ≤ 375 °C. The temperatures at the feed inlet and the product outlet were monitored during the catalytic activity test. The augmented temperatures at the feed inlet were 1 °C, 8 °C, 10 °C, 8 °C and 9 °C, and at the

product outlet, the augmented temperatures were 1 °C, 10 °C, 10 °C, 8 °C and 9 °C at the set furnace temperatures of 300 °C, 350 °C, 375 °C, 400 °C and 450 °C, respectively.

Fig. 5 shows that the CO conversion and CH_4 selectivity as a function of GHSV. The GHSV varies from 5000 to 40,000 h^{-1} . The furnace temperature was controlled at 375 °C and N_2 was fed at a rate of 0.12 $\text{Nm}^3 \text{h}^{-1}$ as the coolant during the test of the GHSV effect. WGS reaction is reversible and one possible method of enhancing the reaction rate is to remove one of the products. Table 1 shows that the selectivities of H_2/CO , H_2/CO_2 and H_2/CH_4 , which were measured at 373 K and pressure difference of 100 kPa, were 2.78, 2.75 and 1.85 respectively. It means that H_2 passed the catalytic nickel plates faster than other gases. It can be seen that the catalytic nickel plate promoted the reaction due to the shift of the equilibrium caused by the difference in the permeation rates between H_2 and the other gases at low GHSV ($\leq 10,000 \text{ h}^{-1}$). Both the CO conversion and the CH_4 selectivity decreased with an increase of the GHSV. Tonkovich et al. [18] reported that the CH_4 selectivity increased with the increase of the contact time in the WGS reaction with Ru/ZrO_2 powder catalyst at 300 °C. Similar to conducting the test as a function of the furnace temperature, the temperatures at the feed inlet and the product outlet were monitored during the GHSV effect test. The augmented temperatures at the feed inlet

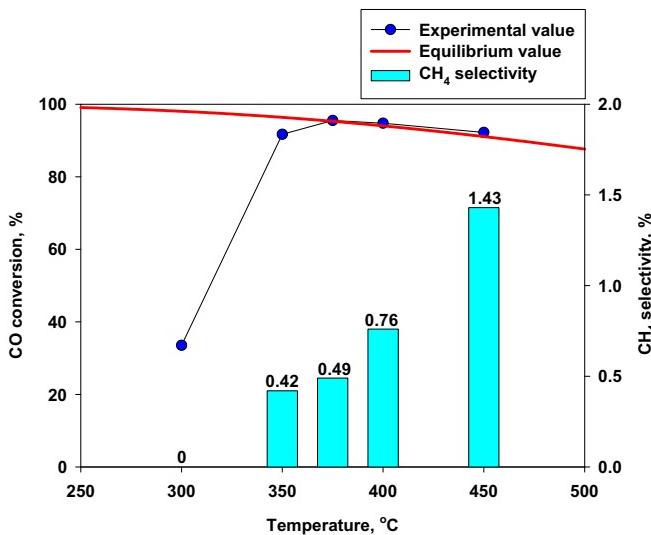


Fig. 4. CO conversion and CH₄ selectivity as a function of the furnace temperature. GHSV: 10,000 h⁻¹; coolant (N₂) flow rate: 0.12 Nm³ h⁻¹.

were 5 °C, 9 °C, 11 °C and 26 °C, and at the product outlet, they were 4 °C, 10 °C, 19 °C and 40 °C at a GHSV of 5000, 10,000, 20,000 and 40,000 h⁻¹, respectively. This result means that the heat from the exothermic WGS reaction increased as the reactant mass increased. As expected, the augmented heat increased with the increase of the reactant mass. Because the WGS reaction is exothermal reversible, CO conversion is thermodynamically favoured at low temperatures. This means that the decrease in the CO conversion at a high GHSV is due to the integrated heat in the reactor. From the GHSV effect test, it can be concluded that 0.12 Nm³ h⁻¹ of N₂ is not sufficient as a coolant for a high GHSV (~40,000 h⁻¹).

3.3. Coolant effect

Because the equilibrium conversion decreases with increasing temperatures for an exothermic reaction, proper heat removal is required in an exothermal reaction system. In an exothermal reaction, higher conversion can be achieved for adiabatic operation by connecting the reactors in series with interstage cooling [9,27]. Recently, a pinch analysis study showed that two coolers were required to completely remove the heat from the WGS reactor

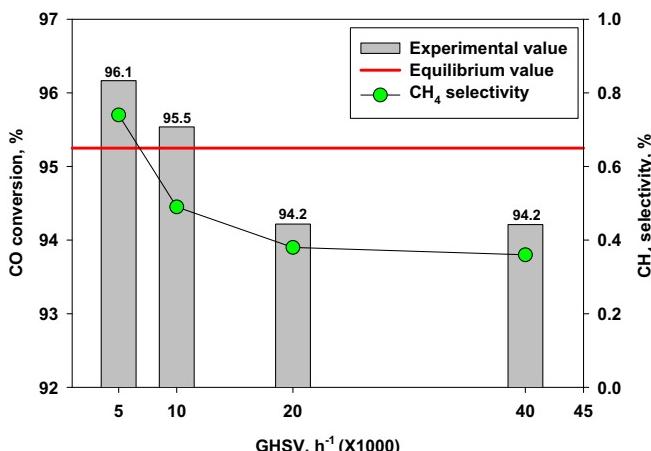


Fig. 5. CO conversion and CH₄ selectivity as a function of GHSV. Furnace temperature: 375 °C; coolant (N₂) flow rate: 0.12 Nm³ h⁻¹.

Table 1
H₂/gases selectivities of the catalytic nickel plate.

	H ₂ /CO	H ₂ /CO ₂	H ₂ /CH ₄
Selectivity	2.78	2.75	1.85

product stream [16]. Martelli et al. suggested the use of an advanced ECN WGS unit in an IGCC plant for thermodynamically and economically favourable operation, especially in the case of syngas cooling for the WGS reactor [28]. The advanced ECN process consists of four sequential, adiabatic shift reactors, each of which is fed a fraction of the original syngas stream and the required amount of steam. From the GHSV effect test, we concluded that 0.12 Nm³ h⁻¹ of N₂ is not sufficient as a coolant for the operation at high GHSV. In this section, the feed flow rate of the coolant was verified to control the generated heat in the WGS reaction and the temperatures at each point for the CO conversion and CH₄ selectivity were monitored at a GHSV of 40,000 h⁻¹. The profile of the temperatures at the feed inlet, product outlet, coolant inlet and coolant outlet is displayed in Fig. 6. During the coolant flow rate effect test, the furnace temperature was set at 375 °C. At the beginning of the WGS test with a coolant of 0.03 Nm³ h⁻¹, the temperature of the reactant inlet decreased rapidly because the reactants were fed at room temperature. Then, the temperatures at the four points increased after ~20 min because of the heat generated by the WGS reaction. The temperatures of the feed inlet and product outlet reached to 389 °C and 409 °C after ~1 h. As the coolant flow rate increased from 0.03 Nm³ h⁻¹ to 0.24 Nm³ h⁻¹, the temperature of the product outlet decreased to 390 °C and the temperature deviation between the feed inlet and the product outlet decreased from 20 to 8.5 °C. It means that the heat generated from the WGS reaction was sufficiently controlled by the coolant flow rate. The CO conversion and CH₄ selectivity as a function of the coolant flow rate is displayed in Fig. 7. The CO conversion increased with increasing the coolant flow rate and almost reached the equilibrium value at 375 °C at a coolant flow rate of 0.24 Nm³ h⁻¹, while the CH₄ selectivity remained ~0.4%. From the coolant flow rate effect test, we can conclude that the newly designed single-stage

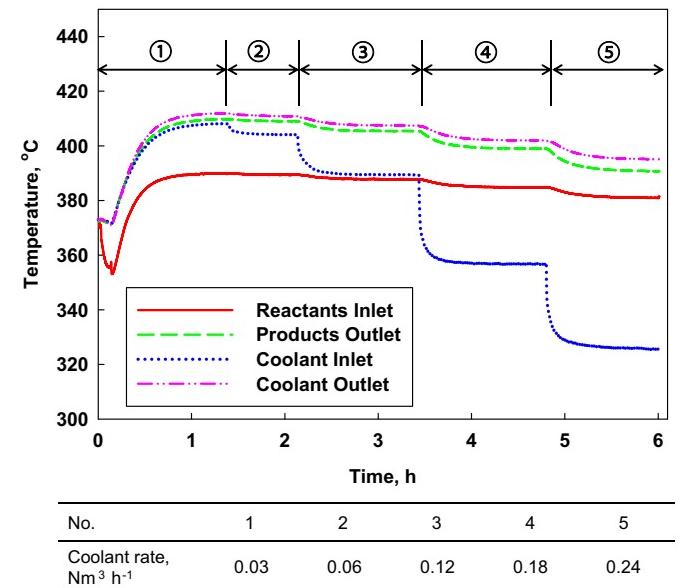


Fig. 6. Temperature profiles as a function of the reaction times with variation of the coolant flow rate at GHSV of 40,000 h⁻¹. Furnace temperature: 375 °C.

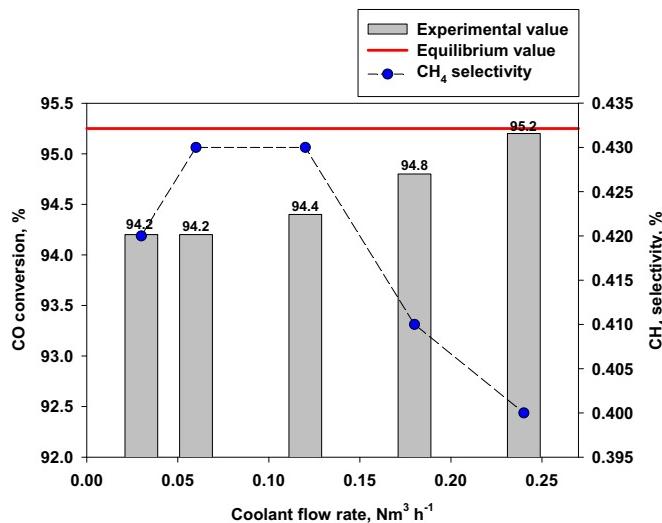


Fig. 7. CO conversion and CH_4 selectivity as a function of the coolant flow rate. GHSV: 40,000 h^{-1} ; furnace temperature: 375 °C.

temperature-controllable reactor allows operation with a minimised temperature gradient in an exothermic WGS reaction.

4. Conclusions

The following results were obtained from the WGS tests using our newly designed single-stage temperature-controllable reactor:

- The reactor was newly designed to control the temperature of the catalyst bed in a single stage for the exothermic WGS reaction to prevent catalyst deactivation and side reactions, such as a methanation reaction.
- The WGS activation test as a function of the furnace temperature at GHSV of 10,000 h^{-1} was carried out and showed that the CO conversion increased to its equilibrium value at 375 °C. Furthermore, at the furnace temperature of ≥ 400 °C, the CO conversion slightly exceeded the equilibrium value because of the methanation reaction. The CH_4 selectivity remained very low at $\leq 0.5\%$ at the furnace temperature of ≤ 375 °C.
- As the GHSV increased from 5000 to 40,000 h^{-1} at the furnace temperature of 375 °C and N_2 at a flow rate of 0.12 $\text{Nm}^3 \text{h}^{-1}$ as the coolant, CO conversion decreased below the equilibrium value and the augmented temperature at the feed inlet was increased from 5 °C to 26 °C, and the temperature at the product outlet was increased from 4 to 40 °C because the heat from the exothermic WGS reaction increased as the reactant mass increased.
- At a GHSV of 40,000 h^{-1} , the CO conversion increased with an increase in the coolant flow rate, and it nearly reached the

equilibrium value of 375 °C at a coolant flow rate of 0.24 $\text{Nm}^3 \text{h}^{-1}$, while the CH_4 selectivity remained at $\sim 0.4\%$.

- The WGS test with the newly designed single-stage temperature-controllable reactor showed that this reactor allowed operation with a minimised temperature gradient in an exothermic WGS reaction.

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